120AQ

Separation and Characterization of Petroleum Hydrocarbons and Surfactant in Orimulsion Dispersion Samples

Zhendi Wang and Merv Fingas
Emergencies Science Division
ETC, Environment Canada
3439 River Road, Ottawa, Ontario
Canada, K1A 0H3

"Separation and Characterization of Petroleum Hydrocarbons and Surfactant in Orimulsion Dispersion Samples", In Proceedings of the Nineteenth Arctic Marine Oilspill Program Technical Seminar, Environment Canada, Ottawa, pp 115-135, 1996.

ABSTRACT

Orimulsion is an oil-in-water emulsion, into which a nonionic surfactant has been added in order to stabilize the emulsion. Many countries have shown great interest in this new bitumen-based fuel because of its competitive price, guaranteed long-term supply, and no need for major infrastructure changes for use in existing power stations. In view of the increasing importance of Orimulsion as an alternative fuel, it becomes necessary to have a better understanding of its physical properties, chemical composition, and toxicity to aquatic organisms. This paper reports detailed separation and characterization results of petroleum hydrocarbons and surfactant in Orimulsion dispersions. A membrane filtration method has been developed and applied for separation of oil particulates from surfactant-water phase of Orimulsion dispersion samples which were used for fish toxicity tests. The separated oil particulates were analysed using GC-MS and GC-FID. GC analysis results demonstrate that (1) the saturates in Orimulsion are dominantly composed of GC-unresolvable aliphatic hydrocarbons; (2) Orimulsion does not contain BTEX and lighter alkylbenzenes, and concentrations of alkylated PAHs are low, relative to most crudes; (3) the concentrations of biomarker compounds are significantly higher than most oils. The HPLC technique was used to identify and quantify the nonionic surfactant in the water phase. The surfactant was identified as polyethoxylated nonylphenol with oligomers having ethylene oxide (EO) number ranging from 8 to 24 (average EO = 20). The surfactant concentration in the source Orimulsion was estimated to be around 0.5%.

INTRODUCTION

Interest in new fuels is strong among many utility and industrial power operators as a result of both economics and shortage of petroleum. Orimulsion is one of these new fuels. Orimulsion is a trade name given to a new liquid fuel (an oil-in-water emulsion) produced in Venezuela, into which a nonionic surfactant is added in order to stabilize the emulsion and render its viscosity similar to heavy fuel oil (HFO). Many countries, particularly US, Canada and Great Britain, have shown great interest in this new bitumen-based fuel, because no major infrastructure changes are required (only some modifications to existing fuel transport, handling, and storage systems are required) to use this new fuel in existing HFO-fired power stations. Orimulsion is not classified by OPEC as a conventional crude oil and will therefore not be affected by Venezuela's OPEC production and export quota. Another attraction is that the producer of Orimulsion, Petroleos De Venezuela SA (PDVSA), offers long-term contracts of 15-20

years with the price of the product adjusted in line with any changes in the price levels of steam coal, its main competitor in the fuel market.

In September 1988, the New Brunswick Power Commission of Canada launched Orimulsion into the commercial testing market by adapting one of its 100 MW units at Dalhousie to use the new fuel. The New Brunswick Power Commission has signed a 20-year contract with PDVSA. The first delivery of Orimulsion took place in early 1994. Since 1988, several reports and reviews on physical properties, experimental spills, spill modelling, and marketing strategies of Orimulsion have been published [1-5]. However, no comprehensive study has been conducted and reported on the quantitative chemical composition of Orimulsion, and on separation and analysis of petroleum hydrocarbons and surfactant(s) of Orimulsion. In view of the importance of Orimulsion as an alternative fuel, detailed re-evaluation of physical and chemical properties of Orimulsion, characterization of petroleum hydrocarbons and surfactant(s) in Orimulsion dispersions, and toxicity study of Orimulsion is definitely needed.

In this paper, we report results of separation and characterization of petroleum hydrocarbons and surfactant in Orimulsion dispersions which were used for fish toxicity tests. A membrane filtration method has been developed and applied for separation of Orimulsion oil particulate from the surfactant-water phase of Orimulsion dispersion samples. The separated Orimulsion oil particulates were then re-dissolved and analysed using gas chromatography-mass spectrometry (GC-MS) and capillary GC equipped with flame ionization detector (GC-FID) for determination of total petroleum hydrocarbons (TPH), n-alkane distribution, polycyclic aromatic hydrocarbons (PAHs) and their alkylated homologues, and biomarker terpanes and steranes. High performance liquid chromatography (HPLC) was used to identify and quantify the nonionic surfactant in the water phase.

EXPERIMENTAL

Orimulsion dispersion samples used for fish tests

The Orimulsion dispersions used for fish tests were received from Aquatic Toxicology Section, Environmental Quality Laboratory, Environment Canada, Atlantic Region. The detailed description of the Orimulsion dispersion samples is presented in Table 1. In brief, oil-in-water dispersions (OWD) were prepared by adding Orimulsion to water in various ratios to obtain dispersions with desired concentrations, for example, 25,000 and 7,500 mg/L. The dispersions were then stirred and settled before adding the fish. The dispersion samples were removed from mid-depth in the water column by means of a clean siphon. All were stored in clean 1-L glass jars. The jars were filled with no air space, tightly capped, and stored at 4 ^{0}C until shipping. The samples were stored in a cold room at 4 ^{0}C for analysis after they were received.

The aquatic toxicity results have been reported elsewhere [5].

Surfactants and oils

Surfactants and crude oils were obtained from various sources and stored in a cold room of the laboratory of Emergencies Science Division.

Membrane filtration

A membrane filtration method was developed and used for separation of

Table 1 Description of Orimulsion Dispersion Samples for Fish Toxicity Test

Sample	Sample Description
3	OWD, nominal concentration = 25,000 mg/L, stirred two days, settled 3 hours, for Daphnia magna test
4	OWD, 25,000 mg/L, filtered with 1µm membrane, details as # 3.
5	No oil. Freshwater control (tap water) for Rainbow trout test.
8	OWD, nominal concentration = 7,500 mg/L, start of Rainbow trout test, sampled at 0 hour.
9	OWD, nominal concentration = 7,500 mg/L, termination of Rainbow trout test, sampled 24 hours later.
10	OWD, stirred 3 days, settled 3 days, nominal concentration 25,000 mg/L, 100% test solution for start of Rainbow trout test, sampled at 0 hour.
11	OWD, as for # 10, termination of Rainbow trout test, sampled 24 hours later.
12	OWD, stirred 3 days, settled 3 days, nominal concentration = 25,000 mg/L, 1% test solution for start of Rainbow trout test, sampled at 0 hour.

* OWD : oil-in-water dispersion

Orimulsion oil particulates from the surfactant-water phase. The detailed membrane filtration procedures are described as follows:

-the jars were vigorously shaken for 5 minutes before sampling, because Orimulsion tends to settle in fresh water;

-10.0 mL of the well-shaken samples was immediately transferred from the mid-depth of the bottle to a pre-prepared filter funnel by means of a clean disposable pipet. For #4 (1-μm pre-filtered) and #12 (1% test solution), 200 mL of samples were transferred and filtered. For #5 (freshwater control), a liquid-liquid extraction technique was applied to extract any possible hydrocarbons from 1-L of the sample;

-samples were filtered by vacuum through the Supelco (Bellefonte, PA) Nylon 66 0.45 μm membrane, by which the Orimulsion oil particulates were separated from the surfactant-water phase and were trapped on the membrane. The clean and colourless filtered surfactant-water solution was used for surfactant analysis by HPLC;

-the Orimulsion oil particulates were completely transferred to a beaker by dichloromethane (DCM), and the Orimulsion oil solutions in DCM were then dried by passage through anhydrous sodium sulphate;

-the dried Orimulsion oil solutions were concentrated by rotary evaporation and solvent-exchanged to hexane phase, and were then made up to an appropriate volume;

-aliquots of the concentrated Orimulsion oil hexane solutions were blown down with nitrogen to residues and weighed on a microbalance to obtain total solvent-extractable materials (TSEM).

Column chromatographic fractionation of Orimulsion extracts

The microcolumn fractionation technique was employed for sample cleanup and fractionation of the concentrated Orimulsion extracts [6-8]. Appropriate aliquots of extracts (containing TSEM ~ 20 mg) were applied to the 3-gram silica gel column which had been preconditioned with 12 mL of hexane. Half of the hexane fraction (F1) was used for analysis of saturates and biomarker compounds; half of the 50% benzene fraction (F2) was used for analysis of target PAHs and alkylated PAH homologues. The remaining half of F1 and F2 was combined (F3) and used for the determination of total hydrocarbons (TPH). These three fractions were concentrated under a stream of nitrogen to appropriate volumes, spiked with internal standards, and then adjusted to accurate pre-injection volumes for GC analysis.

Capillary gas chromatography (GC) and gas chromatography-mass spectrometry (GC/MS)

Analyses for n-alkane distribution and total petroleum hydrocarbons (TPH) were performed on a Hewlett-Packard (HP) 5890 gas chromatograph equipped with a flame-ionization detector (FID) and an HP 7673 autosampler. A 30-m x 0.32-mm id. (0.25-μm film) DB-5 fused silica capillary column (J&W, Folsom, CA, USA) was used. The carrier gas was helium (2.5 mL/min). The injector and detector temperatures were set at 290 °C and 300 °C, respectively. The following temperature program was used: 2-min hold at 50 °C; ramp to 300 °C at 6 °C/min; and 16-min hold at 300 °C. A 1-μL aliquot was injected in the splitless mode with a 1-min purge-off.

Analyses of target polycyclic aromatic hydrocarbons (PAHs) and biomarker compounds were performed on an HP Model 5890 GC equipped with a Model HP 5972 mass selective detector (MSD). System control and data acquisition were achieved with

an HP G1034C MS ChemStation (DOS series). The MSD was operated in the scan and selected ion monitoring (SIM) mode modes for identification of components, and in the SIM mode for quantitation of target compounds. An HP-5 fused-silica column with dimensions of 30-m x 0.25-mm id. (0.25-μm film) was used. The chromatographic conditions were as follows: carrier gas, helium (1.0 mL/min); injection mode, splitless; injector and detector temperature, 290 °C and 300 °C respectively; temperature program for target PAHs, 90 °C for 1-min, ramp to 160 °C at 25 °C/min and then to 290 °C at 8 °C/min, and hold 15-min; temperature program for alkylated PAHs and biomarker compounds, 50 °C for 2-min, ramp to 300 °C at 6 °C/min and hold 16 min.

High performance liquid chromatography

The analysis of surfactant was performed on a Shimadzu system (Columbia, MD) consisting of two LC-610 pumps, an SCL-6B system controller and a variable-wavelength SPD-6AV UV-VIS detector. The chromatograms with peak area and retention times were recorded on a Shimadzu CR-501 Chromatopac integrator.

The chromatographic separation was carried out isocratically in the reversed-phase mode with a 150 mm x 4.6 mm id. stainless C1 TMS column (particle size 5 μm) purchased from Chromatography Sciences Co. (Montreal, Canada). After trial of various conditions, the mobile phase used was a mixture of HPLC-grade methanol and deionized water (60:40, v/v). The column effluent was monitored at 220 nm (deuterium lamp, flow cell volume 8 μL), which corresponds to the maximum absorption of the surfactant used for Orimulsion. The flow rate was maintained at 1.0 mL/min and the column was maintained at ambient temperature (22 ± 1 °C). The injection system was a Rheodyne Model 7125 sample injector equipped with a 20-μL sampling loop.

All solvents used were chromatographic grade and were used without further purification.

RESULTS AND DISCUSSION

Characterization of petroleum hydrocarbons in Orimulsion

Table 2 summarizes the hydrocarbon analysis results for the Orimulsion dispersion samples by gravimetric and GC/FID methods. In addition to the TSEM and GC-determined TPH, ratios of saturates/TSEM, aromatics/TSEM, UCM/TPH, and TPH/TSEM are also listed in Table 2. UCM is defined as the unresolved hydrocarbon mixture detected by GC, which appears as the "envelope" or "hump" area between the solvent baseline and the curve defining the base of the resolved peaks. For comparison, the hydrocarbon analysis results for the duplicate source Orimulsion samples are also presented in Table 2. Figure 1 presents the GC/FID chromatograms for total petroleum hydrocarbon analysis.

Key points from Table 2 and Figure 1 are summarized as follows: (1) the most pronounced feature of Orimulsion composition is that the unresolved complex mixture dominates the total GC peak area, that is, the saturates in Orimulsion are mainly composed of GC-unresolvable aliphatic hydrocarbons; (2) the ratios of UCM/TPH are exclusively higher than 98% for all samples including the source Orimulsion samples, and no GC-resolved n-alkane peaks including isoprenoids such as pristane and phytane were detected. Only when higher sensitivity GC/MS (in SIM mode, m/z = 85) is used to analyse F1, could very small peaks of n-alkanes from C_{11} to C_{15} be distinguished

Table 2 TSEM and TPH Values for the Orimulsion Samples

Sample	Start Conc. of Orimulsion (mg/L)	Start Conc. of oil after correction of H2O content (mg/L)	TSEM (mg/L)	GC-TPH (mg/L)	GC-Saturates (mg/L)	Saturates in TPH (%)	Aromatics in TPH (%)	UCM/TPH (%)	TPH/TSEM (%)
3	25,000	18,250	5,500	1,623	840	52	48	98	30
4	1µm pre-filter		ND*	0.065					
5	fresh water control		ND*	0.030					
8	7,500	5,475	4,100	1,390	690	50	50	98	33
9	7,500	5,475	2,300	802	426	53	47	98	35
10	25,000	18,250	5,400	1,766	822	47	53	98	33
11	25,000	18,250	3,500	1,190	590	50	50	98	34
12	250	183	35	12	8	57	43	98	34
Ref.1**	1.0g	0.73g		323 mg/g oil	140 mg/g oil	52	48		32
Ref.2**	1.0g	0.73g		332 mg/g oil	141 mg/g oil	51	49		33

* ND : Not determined due to very small quantity of extractable material

** The values for Ref.1 and Ref.2 were obtained from direct analysis of duplicate Orimulsion samples. The average water content in Orimulsion was determined to be 27% by Karl Fischer titration. The values of TPH and Saturates given in the table are the values (mg/g oil) after correction of water content.

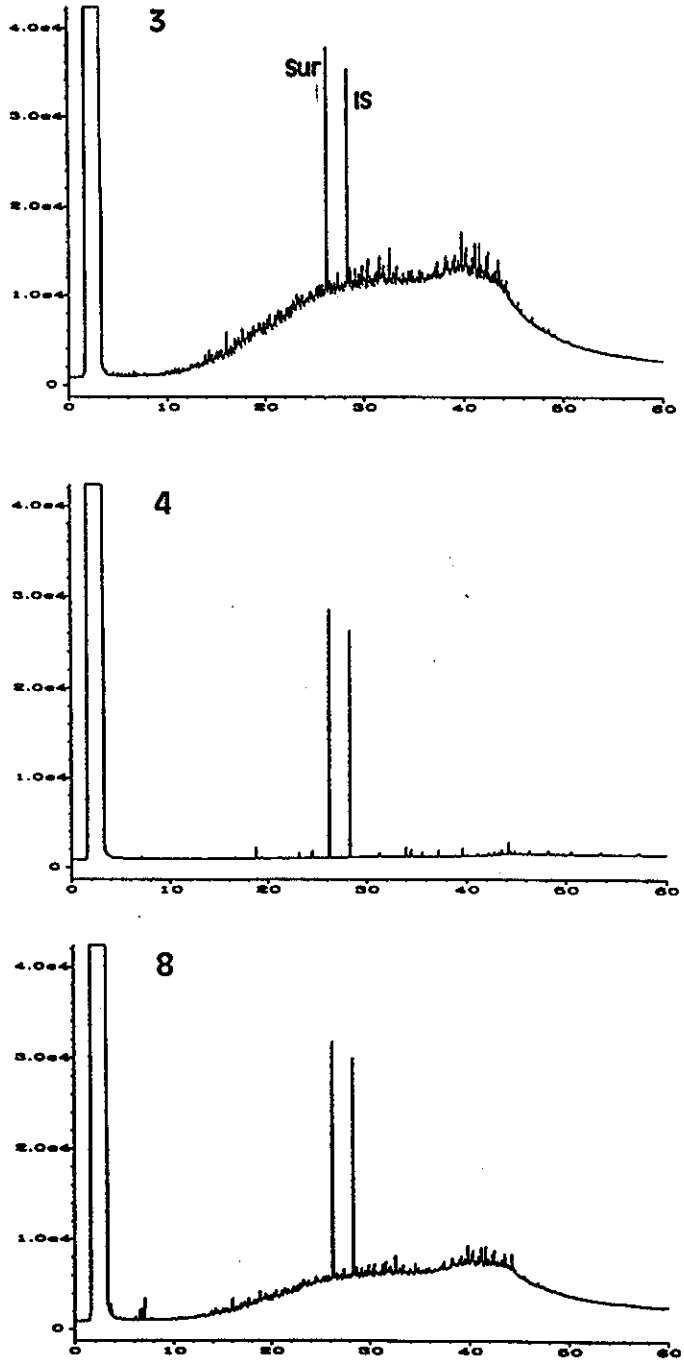

Figure 1 GC/FID chromatograms for total petroleum hydrocarbon analysis of Orimulsion dispersion samples #3, #4, and #8. Sur and IS represent surrogate and internal standard respectively.

(Figure 2). The whole chromatographic profiles of Orimulsion look like that of extremely highly weathered and degraded crudes; (3) the TPHs (saturates plus aromatics) are only 30-35% of the total weight of TSEM, indicating relatively high portion (~70%) of resins and asphaltenes in Orimulsion. This result is understandable because one significant feature of Bitumen-type oil is the high percentage of resin and asphaltenes in the oil; (4) the aromatics are approximately 50% of the TPH for all samples, far higher than the values of aromatics % for light and medium crudes.

Compared to sample #8 (its starting nominal concentration is 7,500 mg/L, measured TSEM = 4100 mg/L), the TSEM values determined for samples #3, #10 and #11 (their starting nominal concentrations are 25,000 mg/L, TSEM values are 5,500, 5,400, and 3,500 mg/L, respectively) are much lower than expected. Repeated analyses give roughly the same results. The most possible reason for this may be that the samples were not uniform before sampling due to 3 hours settling time for #3, and 3 days settling time for #10 and #11, respectively (see Table 1 for sample description). Some concentration gradient would be expected because Orimulsion tends to settle in water.

Sample #4 showed a extremely low value of TPH, demonstrating that the 1 μm membrane can effectively remove almost 100% of Orimulsion oil particulates from the surfactant-water phase;

At the point of termination of the Rainbow trout test (24 hour duration), the concentrations of TPH for #9 and #11 were determined to be 802 mg/L and 1190 mg/L, 42% and 33% lower than the TPH concentrations for the corresponding starting samples #8 and #10, respectively. That means that the test fish was killed due to consumption, absorption and adsorption of Orimulsion (possibly by both petroleum hydrocarbons and surfactant) during the toxicity test. As the toxicity study concluded, "a spill of Orimulsion will result in a higher exposure to oil, and therefore a higher risk to aquatic organisms than would a spill of heavy fuel oil" [5].

Figure 3 shows the GC/MS total ion chromatograms in the SIM mode for the alkylated PAHs. Table 3 summarizes analysis results of the 5 target alkylated PAH series and diagnostic ratios of the "source-specific-marker" PAH compounds [9]. As an example, Figure 4 depicts graphically the distribution of alkylated PAHs for the source oil and sample #3. Note that the total PAHs in Table 3 are expressed in both μg/g TSEM and mg/L of H_2O. TSEM gives a reasonably equal basis for the determination of the relative composition changes of hydrocarbons in Orimulsion samples. It is only by this way that the quantitation results are comparable.

The sum of the 5 target alkylated PAHs was determined to be in the range of 2300-2900 μg/g of TSEM. Major alkyl PAH composition characteristics are outlined as follows: (1) compared to most crude oils, the concentrations of the total of 5 target alkylated PAHs in Orimulsion are low; (2) Orimulsion does not contain BTEX (the collective name of benzene, toluene, ethylbenzene, and the xylene isomers) and lighter alkylbenzene compounds, evidenced by the fact that no alkylbenzene peaks were detected before the retention time of 15 minutes; (3) the distribution pattern with the alkyl naphthalene and phenanthrene series being the most abundant among the 5 target alkylated PAH series, is observed for the source oil. However, for the fish test oil-in-water dispersion samples, the loss of alkyl naphthalene series relative to the alkyl phenanthrene series is obvious, mainly due to the higher solubility of naphthalenes in water; (4) different from most oils, the distribution abundances of $C_0<C_1<C_2<C_3$ in each alkyl PAH group except for the alkyl chrysene series is very pronounced (for most oils,

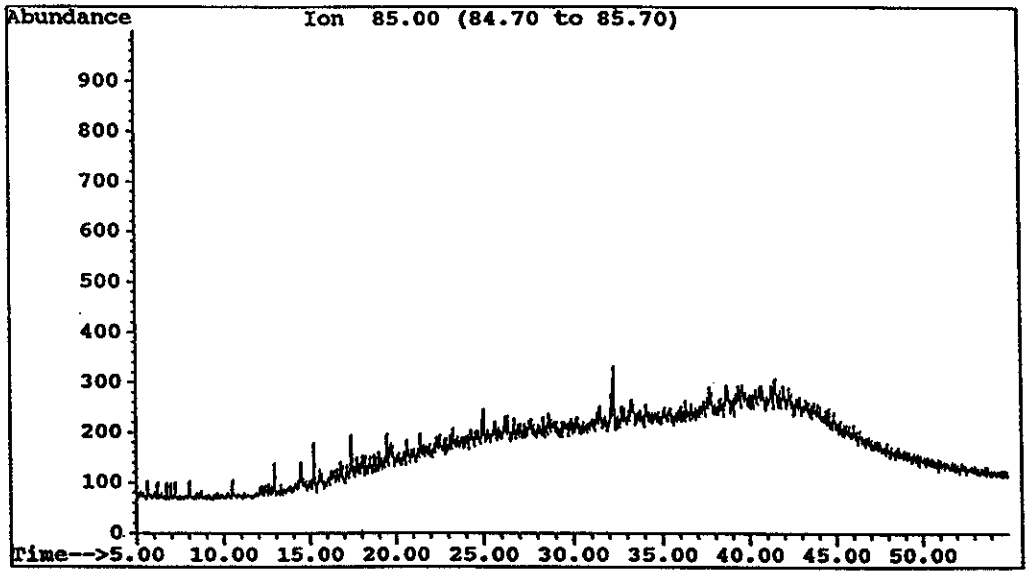

Figure 2 GC/MS chromatogram of saturated hydrocarbons (m/z 85) for the source Orimulsion.

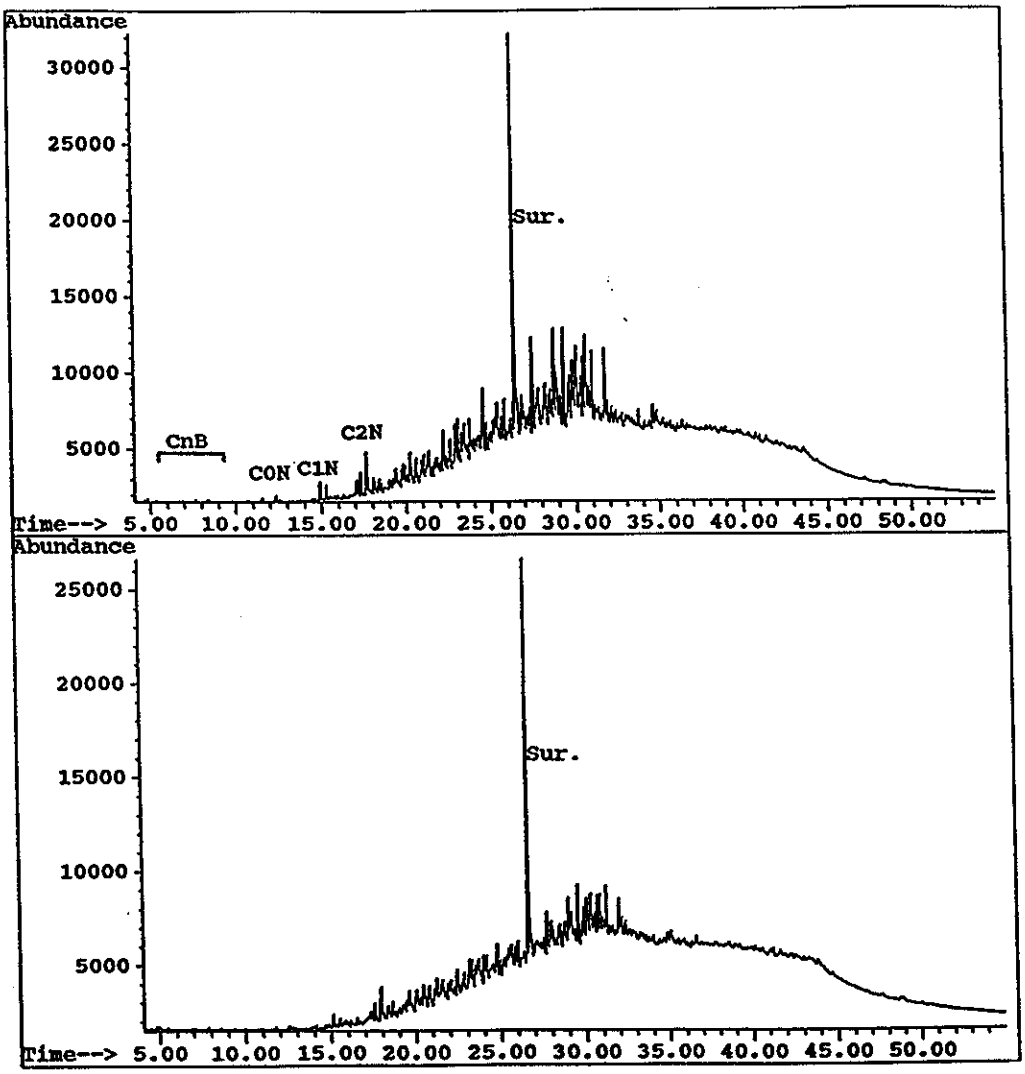

Figure 3 GC/MS total ion chromatograms (in SIM mode) for the alkylated PAHs analysis of the sample #3 (top) and the source Orimulsion (bottom). B and N represent benzene and naphthalene, respectively; n, 0, 1, 2, and 3 represent carbon numbers of alkyl groups in alkylbenzenes and alkylated PAH homologues.

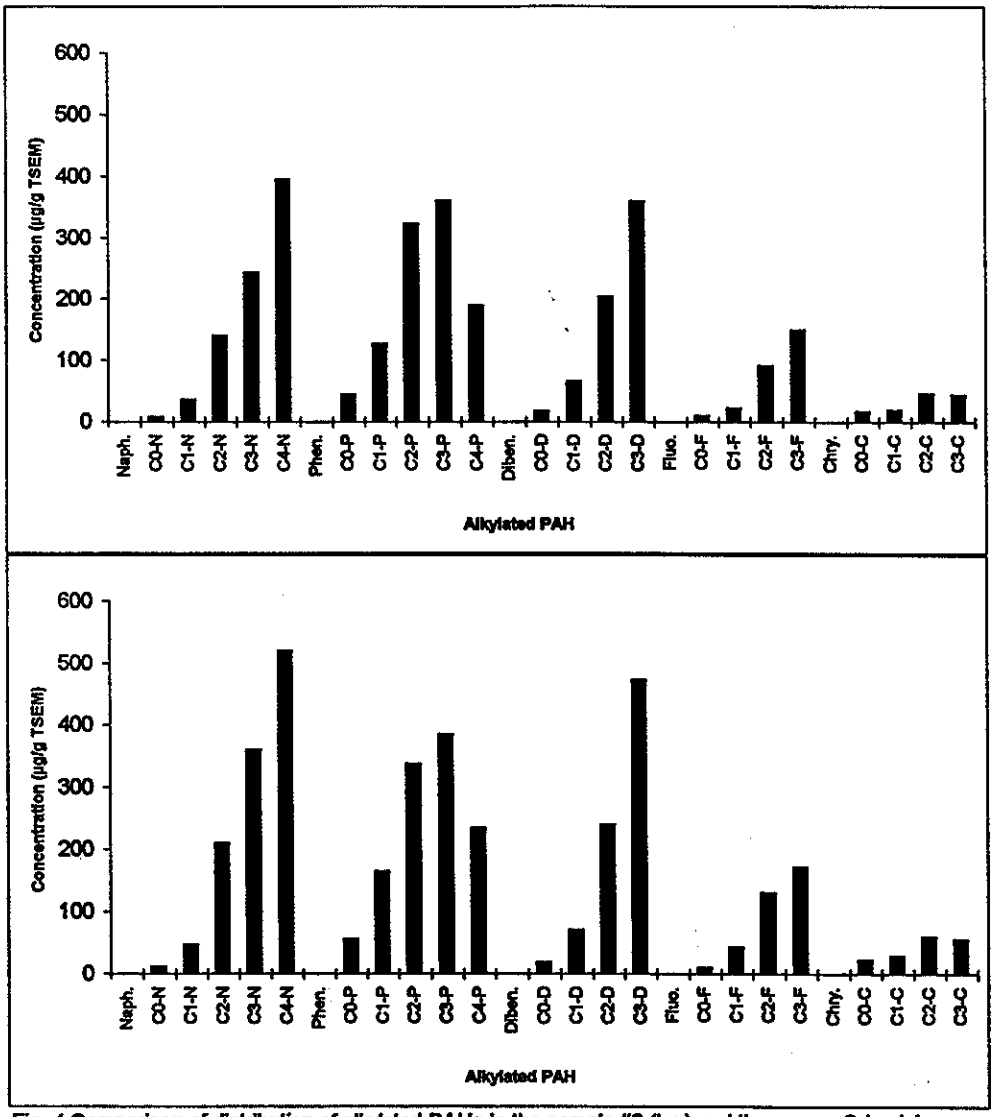

Fig. 4 Comparison of distribution of alkylated PAHs in the sample #3 (top) and the source Orimulsion (bottom). N, P, D, F, and C represent naphthalene, phenanthrene, dibenzothiophene, fluorene, and chrysene, respectively; 0, 1, 2, 3, and 4 represent carbon numbers of alkyl groups in alkylated PAH homologues.

this kind of distribution patterns is seen only when they have been highly weathered).

After the 24 hour Rainbow trout toxicity test, the concentrations of the target PAH homologues were determined to be 7.34 mg/L for #9 and 8.24 mg/L for #11, respectively. Compared to the concentrations of the target PAHs in the corresponding start dispersion samples (11.74 mg/L for #8 and 14.37 mg/L for #10), approximately 1/3 of the target PAHs were reduced, which is in good agreement with the TPH analysis results. Other compositional changes of PAHs are summarized as follows: (1) in general, the alkyl dibenzothiophene and fluorene series did not show changes in their ratios to the alkyl chrysenes compared to the source oil. However, decrease in ratios of the alkyl naphthalene series to the alkyl chrysenes is noticed. This trend is especially obvious for the paired samples #11 and #12 (the ratios of the alkyl naphthalenes to the alkyl chrysenes were determined to be 5.2 and 4.6, respectively), indicating that in addition of being more soluble in water, the alkyl naphthalenes may preferentially be absorbed and/or adsorbed by the test fish; (2) compared to the source Orimulsion (1:0.75:0.92), the changes of the isomeric distribution of 4-, 2-/3-, and 1-methyldibenzothiophene for samples #10 (1:0.24:0.96), #11 (1:0.02:1.08), and #12 (1:0.02:1.08) are pronounced. This may be mainly because of preferential biodegradation of 2-/3-methyldibenzothiophene, resulting in decrease of the ratio relative to 4-methyldibenzothiophene [9].

Compared to most oils, significantly higher amounts of biomarker compounds were detected in the source and the toxicity test Orimulsion samples. For example, the concentrations of C_{23}-terpane and C_{30}-hopane were determined to be in the range of 230-244 and 210-222 μg/g of TSEM. Figure 5 shows distribution profiles of biomarker terpanes at m/z 191 for the source oil and sample #8. The terpane distribution reflects the petroleum inputs. Figure 5 is characterized by the terpane distribution in a wide range from C_{20} to C_{35} with C_{23} to C_{24} tricyclic terpanes and C_{29} to C_{30} αβ-pentacyclic hopanes being the most prominent. The GC/MS measurements demonstrate that the profiles and patterns of the m/z 191 and 217 (the steranes are mainly dominated by C_{27}, C_{28}, and C_{29} 20R/20S sterane compounds) ion chromatograms of the samples are identical to each other and to the source oil. In addition, the biomarker compounds of the Orimulsion samples did not show any noticeable changes in their absolute concentrations in comparison to the source oil, and the ratios of five pairs of target terpanes C_{23}/C_{24}, C_{29}/C_{30}, Ts/Tm, C_{32} 20S/20R, and C_{33} 20S/20R are almost same for all samples as well, indicating the composition of biomarkers is virtually unaltered. No biomarker compounds were detected for the fresh water control #5 and only extremely low concentrations of biomarkers were detected for sample #4 (the concentrations of the most abundant C_{23} and C_{30} were determined to be less than 5 μg/L of water) which was pre-filtered using 1 μm membrane, further confirming that the petroleum particulates in Orimulsion can be effectively separated using membrane filtration technique.

Identification of surfactant in Orimulsion

Orimulsion is simply a trade name in which bitumen content is entirely derived from Venezuela's Orinoco region, and to which the addition of water (as described above, the water content was determined to be 27%) and a surfactant turns its consistency into an emulsion with a viscosity resembling heavy fuel oil. Theoretically speaking, there are two different types of emulsions: oil-in-water emulsions, where the very fine oil-in-water droplets disperse in water phase; water-in-oil emulsions, where the

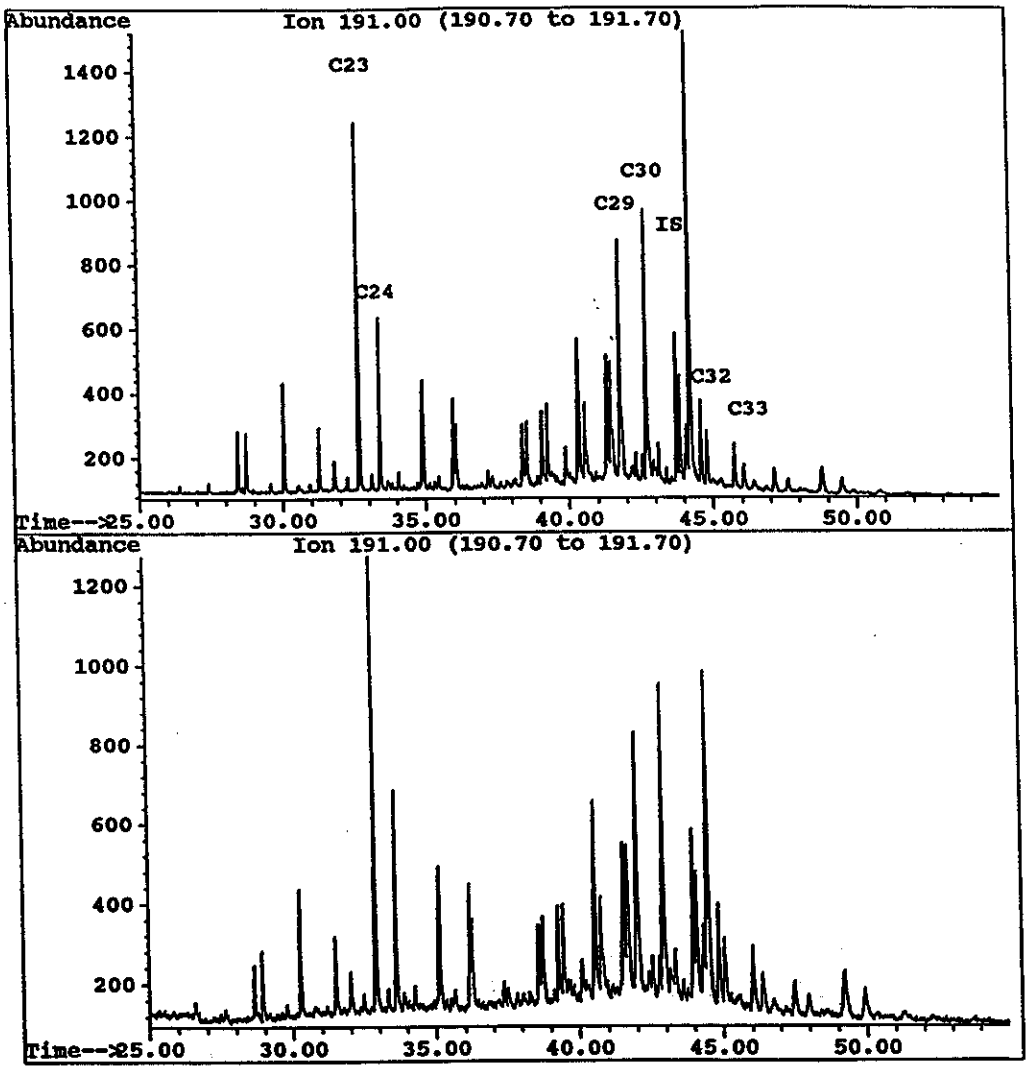

Figure 5 Distribution of biomarker terpanes (m/z 191) in the sample #8 (top) and the source Orimulsion (bottom). IS represents the internal standard. C_{23}, C_{24}, C_{29}, C_{30}, C_{32}, and C_{33} represent C_{23} and C_{24} terpane, C_{29} and C_{30} αβ-hopane, and 20S/20R of C_{32} and C_{33} hopane isomer pairs, respectively.

Table 3 Alkylated PAH Homologue Distribution (µg/g TSEM) and Diagnostic Ratios of PAHS Orimulsion Samples

Conc. & Ratios of PAHs	3	8	9	10	11	12	Source 1	Source 2
Sum of naphthalenes	814.6	785.7	831.4	636.8	523.4	423.8	1141.9	1024.9
Sum of phenanthrenes	1036.3	1031.0	1100.7	1009.0	920.6	890.0	1168.5	1234.2
Sum of dibenzothiophenes	639.8	623.3	687.0	609.3	562.5	588.6	794.5	817.8
Sum of fluorenes	267.9	306.5	318.3	288.2	256.0	276.6	348.2	358.5
Sum of chrysenes	121.2	117.9	127.4	121.0	113.5	114.4	160.1	158.9
Total (µg/g TSEM)	2880	2864	3065	2664	2376	2293	3613	3594
Total (mg/L H_2O)	15.91	11.74	7.34	14.37	8.24	0.08		
Naphs./Chrys.	6.7	6.7	6.5	5.3	4.6	3.7	7.1	6.4
Phens./Chrys.	8.6	8.7	8.6	8.3	8.1	7.8	7.3	7.8
Dibens./Chrys.	5.3	5.3	5.4	5.0	5.0	5.1	5.0	5.1
Fluos./Chrys.	2.2	2.6	2.5	2.4	2.3	2.4	2.2	2.3
4-M-DBT : 2-/3-M-DBT : 1-M-DBT	1 : 0.82 : 0.93	1 : 0.82 : 0.95	1 : 0.80 : 0.90	1 : 0.24 : 0.91	1 : 0.02 : 0.96	1 : 0.02 : 1.08	1 : 0.74 : 0.92	1 : 0.75 : 0.91
C_2D/C_2P : C_3D/C_3P	0.63 : 1.00	0.70 : 0.91	0.63 : 1.03	0.64 : 0.90	0.65 : 0.88	0.72 : 0.96	0.71 : 1.23	0.69 : 1.17

water-in-oil droplets disperse in oil phase. Orimulsion is an oil-in-water emulsion. In order to stabilize the oil-in-water emulsion and prevent the water and bitumen from separation, the surfactant added to Orimulsion has to meet the following criteria: (1) the hydrophilic-lipophilic balance (HLB) value of the surfactant must be high enough; (2) the hydrophillic part of the surfactant molecules must be large enough to be able to dissolve in water (for example, polyethoxylated octylphenol with average ethoxy units smaller than 7 is not dissolved in water and a dispersion forms). Only such surfactant molecules can effectively act by adsorbing at the oil-water interface, forming a molecular film which behaves as a mechanical barrier that protects oil-in-water droplets from coalescence. In addition, as an economical consideration, the surfactant must be inexpensive enough to keep the cost of Orimulsion as low as possible.

The best candidates which can meet such criteria are non-ionic surfactants which have relatively greater number of ethylene oxide (EO) units in the hydrophillic chain of molecules such as, for example, sorbitan ester surfactants, Tween type surfactants, polyethoxylated octylphenols, polyethoxylated nonylphenols, and polyethoxylated amine derivatives [10]. It has been long established that the HLB values increase in direct proportion to the number of EO units of the molecule and that the surfactants having HLB values around 15 can serve well as oil-in-water emulsifiers [10,11]. For example, the HLB values for nonylphenol ethoxylates with EO = 15, 20, and 30 are 15.0, 16.0 and 17.2, respectively. Thus, the range of searching for the best surfactant candidates is greatly narrowed. As for identification of the unknown surfactant(s) used in Orimulsion, it could be achieved through comparison of its HPLC chromatographic pattern and behaviour, and retention times of resolved peaks to those structure-known surfactants.

Figure 6 shows the chromatograms obtained from measurement of the surfactant-water phase of Orimulsion samples #10 and #8. In order to determine the surfactant used in Orimulsion, over 15 possible target nonionic surfactants were studied using HPLC, and their chromatographic characteristics and patterns were carefully examined and compared with that of Orimulsion samples. For examples, Figure 7 presents representative chromatograms of polyethoxylated nonylphenol (EO=20), Tween-20, polyethoxylated cocoamine (EO=15), and Triton X-114. These different types of surfactants show significantly different chromatographic behaviour. But, one common characteristic is that all of these surfactants have relatively high HLB values and relatively larger hydrophillic parts in their molecules (the separation and characterization of sorbitan ester surfactants has been reported elsewhere [12,13]). It can be clearly seen from comparison of Figures 6 and 7 that among all surfactants measured here, the chromatogram of polyethoxylated nonylphenol (EO=20) matches chromatograms of surfactant in Orimulsion samples best. Table 4 summarizes the chromatographic retention times of Orimulsion samples #10 and #8, and polyethoxylated nonylphenol (EO=20) and Triton X-114. It is clear from Table 4 that the retention times of polyethoxylated nonylphenol (EO=20) oligomer peaks match samples #10 and #8 extremely well.

Figure 6, Figure 7, and Table 4 clearly demonstrate that: (1) the chromatographic pattern and profile, the distribution of oligomers of the unknown surfactant in Orimulsion shows great similarity to polyethoxylated (EO=20) nonylphenol, but different from other possible target nonionic surfactants; (2) the retention times of the oligomer peaks with varying EO numbers match to each other extremely well for the

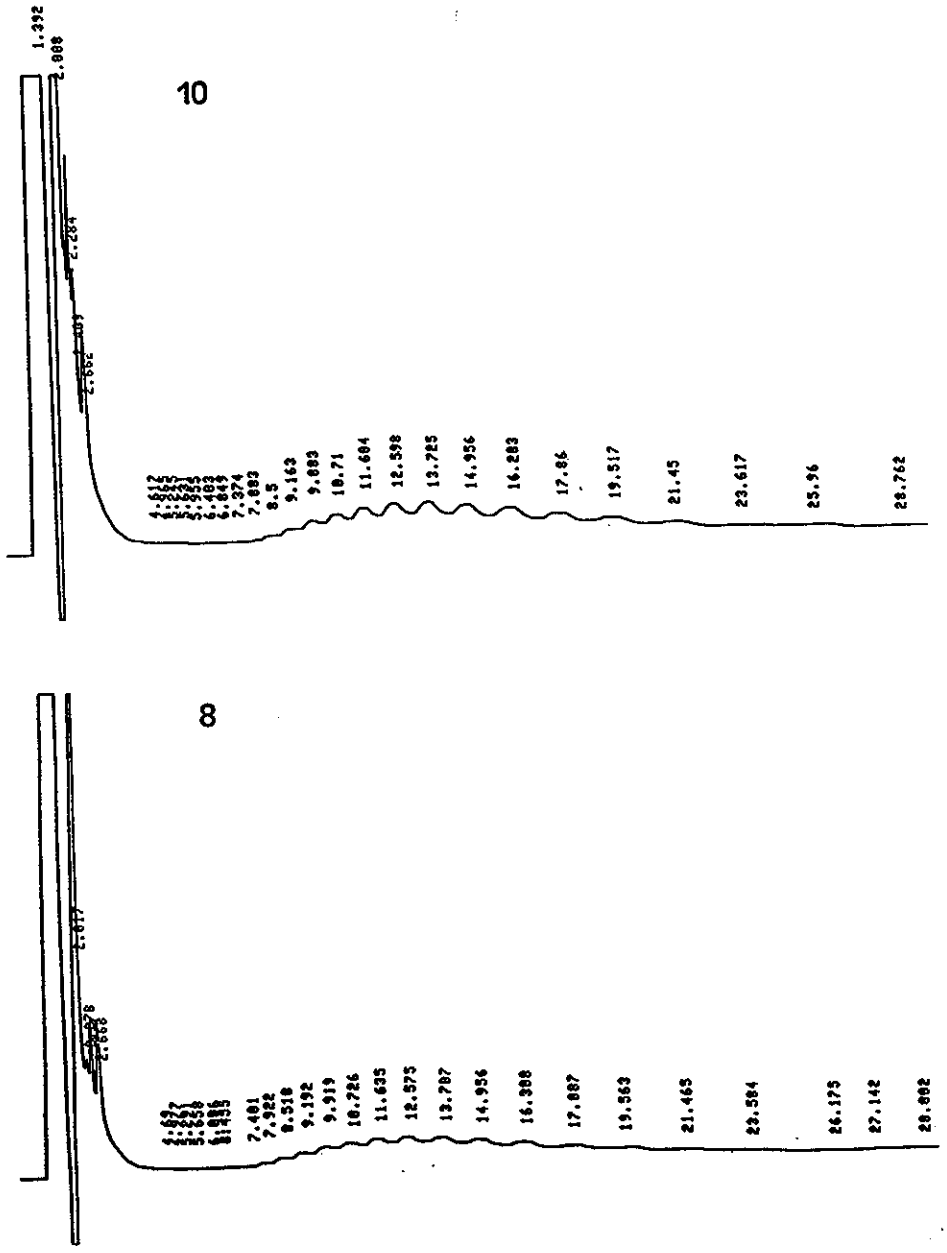

Figure 6 HPLC chromatograms of samples #10 and #8 for surfactant analysis. See chromatographic conditions in "Experimental" section.

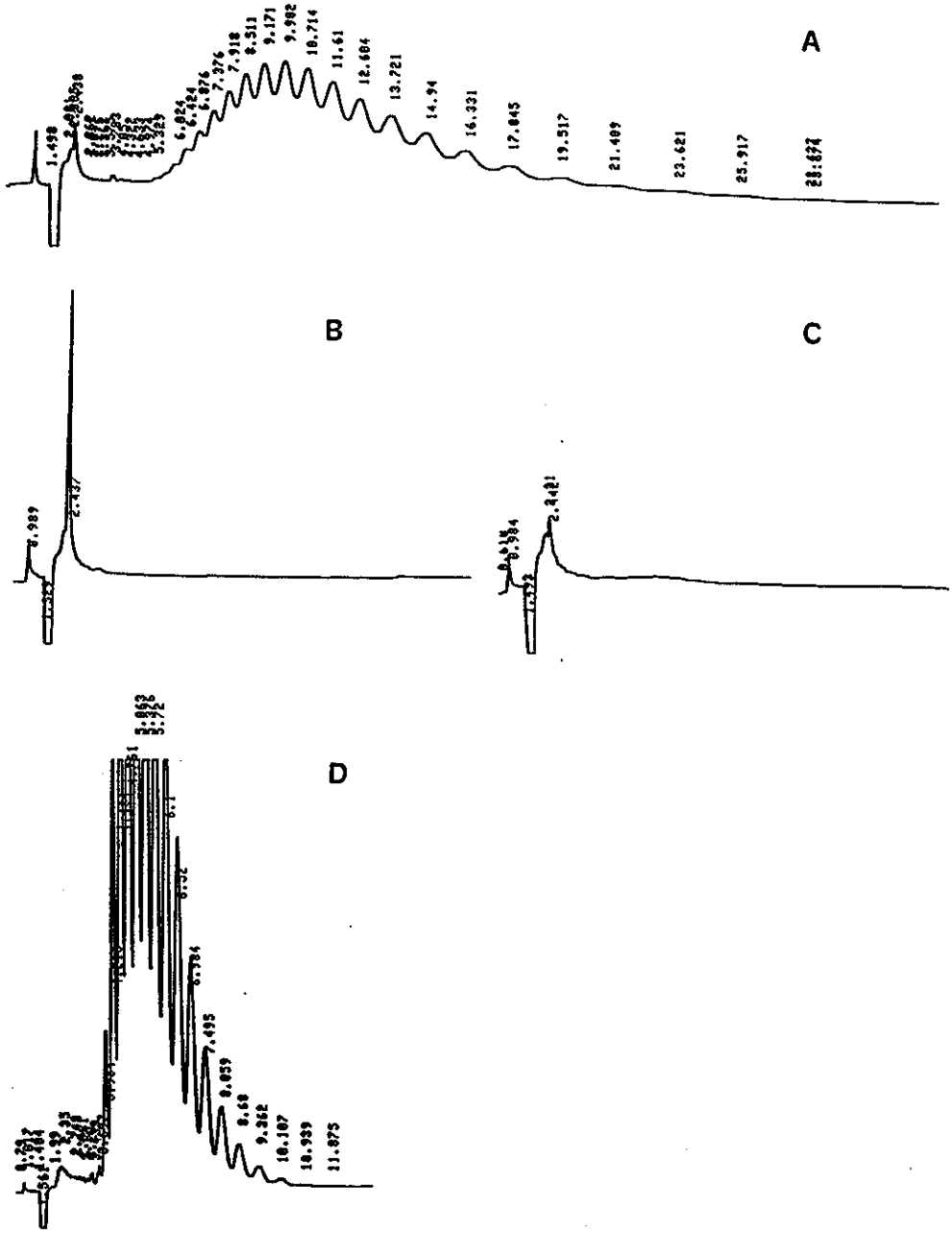

Figure 7 HPLC chromatograms for polyethoxylated nonylphenol (EO = 20) (7A), Tween-20 (7B), polyethoxylated cocoamine (EO = 15) (7C), and Triton 114 (7D).

Table 4 Comparison of HPLC Retention Times of Ori-Surfactant with Polyethoxylated Nonylphenol (EO = 20)

EO Number	Triton X - 114 RT (min.)	EO Number	Polyethoxylated RT (min.)	# 8 Ori-surfactant RT (min.)	# 10 Ori-surfactant RT (min.)
1	3.687	1			
2	3.954	2			
3	4.216	3			
4	4.484	4			
5	4.761	5	6.024		
6	5.063	6	6.024		
7	5.376	7	6.876		
8	5.720	8	7.376	7.374	7.401
9	6.100	9	7.918	7.883	7.922
10	6.520	10	8.511	8.500	8.518
11	6.984	11	9.171	9.163	9.192
12	7.495	12	9.902	9.883	9.919
13	8.059	13	10.714	10.710	10.726
14	8.680	14	11.610	11.604	11.635
15	9.362	15	12.604	12.598	12.575
16	10.107	16	13.721	13.725	13.707
17	10.939	17	14.940	14.956	14.956
18	11.875	18	16.331	16.283	16.308
		19	17.845	17.860	17.887
		20	19.517	19.517	19.563
		21	21.409	21.450	21.465
		22	23.621	23.617	23.584
		23	25.917	25.960	26.175
		24	28.674	28.762	28.802

known and unknown surfactant. Hence, the surfactant used to emulsify Orimulsion is identified to be a polyethoxylated nonylphenol surfactant with average EO number around 20 or greater; (3) The oligomers with EO number from 8 to 24 in the Orimulsion surfactant were characterized. Due to the detection limit and concentration limit, oligomers with EO number smaller than 8 and greater than 24 were not characterized or not detected.

It is noticed that there are several quite large early-eluted peaks (prior to ~4 minutes) in Figure 6, which is thought most probably to be some water-soluble polar and aromatic compounds from oil hydrocarbons. In order to confirm this hypothesis, (naphthalene + benzene)-, hexane-, Cold Lake Bitumen (CLB)-saturated water phase were analysed using HPLC under exact same analytical conditions as for analysing Orimulsion surfactant. The CLB crude was chosen because it has similar physical properties and chemical composition to Orinoco bitumen. Figure 8 presents chromatograms of (naphthalene + benzene)-, hexane-, Cold Lake Bitumen (CLB)-saturated water phase. For comparison purposes, the HPLC chromatogram of water-surfactant water phase of CLB dispersion is also presented in Figure 8. Compared to Figures 5 and 6, one can immediately conclude that those large early-eluted peaks before ~4 minutes in the chromatograms are from Orinoco crude components, and not from the added surfactant. These oil components are most probably aromatic and polar compounds, which have certain solubilities in water and are almost not retained by the column due to their relatively high polarity. Fortunately, they do not affect characterization and quantitation of surfactant oligomers.

Estimation of concentration of the surfactant used for Orimulsion

Because of lack of Venezuela Orinoco crude, the CLB crude was applied as the reference oil to estimate the recovery of polyethoxylated nonylphenol (EO=20) from CLB-surfactant emulsion after passage through the Supelco Nylon 66 0.45 μm membrane. The procedures used to estimate the recoveries of ethoxylated nonylphenol (EO=20) are as follows: (1) 0.25 g of CLB crude and 2.50 mg of polyethoxylated nonylphenol (EO=20), approximately 1% of the crude, were weighed and 10 mL of HPLC grade water was added; (2) the mixture was vigorously shaken for 30 minutes, then was filtered through 0.45 μm Nylon 66 membrane. The oil particulates which stayed on the membrane were discarded, the clean colourless surfactant-water phase was diluted to 50 mL, and the diluted surfactant solution was then injected to the HPLC for surfactant quantitation (see Figure 8); (3) 0.05 mg/mL of the reference polyethoxylated nonylphenol (EO=20) water solution was directly injected into the HPLC under the same analytical conditions; (4) triplicate analyses were performed to obtain the average of the total oligomer peak areas; (5) the average of the total oligomer peak areas from samples was divided by the average of total areas from the reference polyethoxylated nonylphenol (EO=20) water solution to determine the recovery of the surfactant.

The average recovery for polyethoxylated nonylphenol (EO=20) was determined to be 64±3% (n=3). The mass loss of the surfactant is believed mainly due to the formation of the non-separative oil-surfactant particulates and adsorption of surfactant molecules on the membrane surface.

The measured recovery factor was then applied to correct and estimate the true concentrations of the surfactant in Orimulsion. The concentration of polyethoxylated nonylphenol in the source Orimulsion is estimated to be around 0.5%.

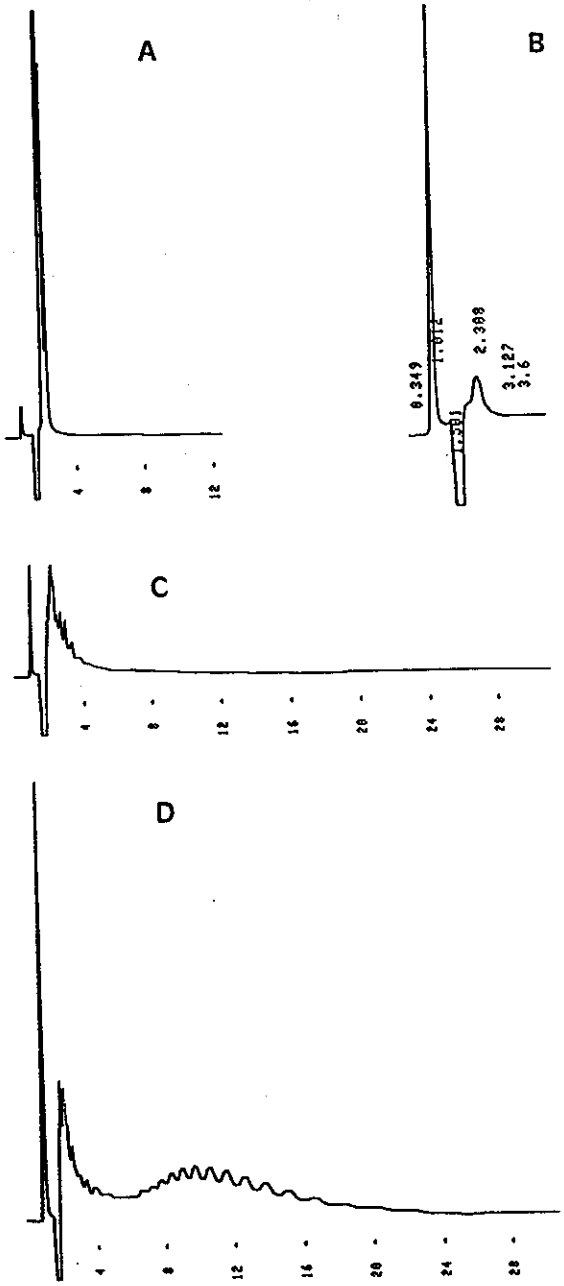

Figure 8 HPLC chromatograms for (benzene + naphthalene)- (8A), hexane- (8B), and Cold Lake Bitumen (CLB)-saturated water phase (8C), and surfactant-water phase of CLB dispersion (8D).

CONCLUSION

A reliable and effective combined method of using membrane filtration, capillary GC, and HPLC techniques has been developed and applied for separation, characterization, quantitation of petroleum hydrocarbons and nonionic surfactant in complicated oil-in-water dispersion samples used for aquatic toxicity tests. The simplicity and directness of the method is obvious. Identification of the surfactant in Orimulsion was achieved by (1) narrowing the searching range based on theoretical considerations and analysis and, (2) comparing chromatographic profiles, oligomer distribution patterns, and retention times of oligomer peaks. The surfactant in Orimulsion was identified as polyethoxylated nonylphenol with oligomers having EO numbers ranging from 8 to 24 (average EO units around 20). The concentration of polyethoxylated nonylphenol in the source Orimulsion was estimated to be around 0.5%.

ACKNOWLEDGEMENT:

The authors would like to thank Mr. Michael Landriault and Mrs. Lise Sigouin for their help in performing the sample cleanup and drawing figures and tables.

REFERENCES

[1] S. L. Ross Environmental Research Limited, *Behaviour and Control of Spills of Orimulsion™*, **1987**.

[2] S. L. Ross Environmental Research Limited, *The Risk, Fate and Behaviour of Orimulsion™ Spills at Dalhousie, N. B.*, **1992**.

[3] Zlantar, M., *Orimulsion: the revolutionary new fuel for power and industry*, Financial Times Business Information, London, **1989**.

[4] BITOR, *Comparative Summary Between Orimulsion Produced by the Primary Emulsification and Dilution Methods*, BITOR, May **1994**.

[5] Jokuty, P.; Whiticar, S.; Fingas, M.; Wang, Z.; Doe, K.; Kyle, D.; Lambert, P.; and Fieldhouse, B. *Orimulsion: Physical Properties, Chemical Composition, Dispersibility, and Toxicity*, September **1995**.

[6] Wang, Z. D.; Fingas, M.; Li, K. *J. Chromatogr. Sci.* **1994**, 32, 361-366.

[7] Wang, Z. D.; Fingas, M.; Li, K. *J. Chromatogr. Sci.* **1994**, 32, 367-382.

[8] Wang, Z. D.; Fingas, M.; Sergy, G. *Environ. Sci. Technol.* **1994**, 28, 1733-1746.

[9] Wang, Z. D. and Fingas, M.; *Environ. Sci. Technol.* **1995**, 29, 2842-2849.

[10] Cross, J. ed., *Nonionic Surfactants: Chemical Analysis*, Marcel Dekker, New York, 1987.

[11] Becher, P. in *Nonionic Surfactants* (M. Schick, ed.), Marcel Dekker, New York, 1967.

[12] Wang, Z. D. and Fingas, M. *HRC*, **1994**, 17, 15-19.

[13] Wang, Z. D. and Fingas, M. *HRC*, **1994**, 17, 85-90.